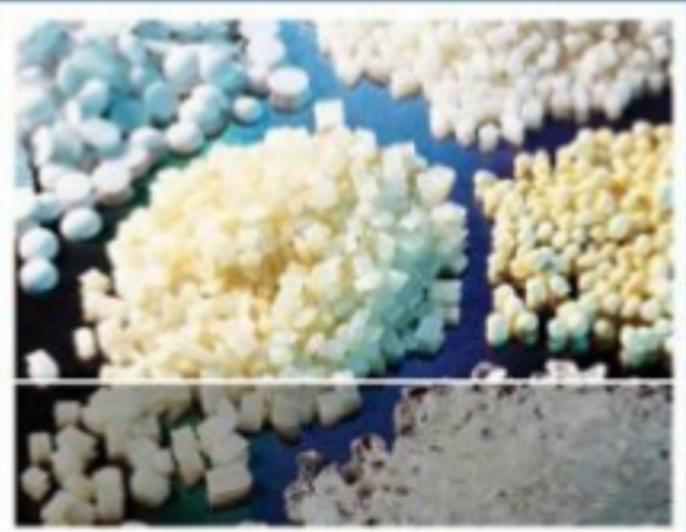


# **EXHIBIT T**

Ralph Maier

Michael Schiller

# Plastics Additives Handbook



6th Edition

HANSER

HANSER

Table of Contents

Plastics Additives Handbook

Herausgegeben von Hans Zweifel, Ralph D. Maier, Michael Schiller

ISBN: 978-3-446-40801-2

For further information and order see

<http://www.hanser.de/978-3-446-40801-2>  
or contact your bookseller.

Hans Zweifel  
Ralph D. Maier  
Michael Schiller

# Plastics Additives Handbook

6th Edition

With contributions by:

S. E. Amos, P. Bataillard, Prof. Dr. N. C. Billingham, Dr. K. Chmil, L. Evangelista,  
G. M. Giacoletto, Dr. B. Gilg, F. Gugumus, W. Hohenberger, A. Holzner, J. H. Horns,  
H. Hurnik, T. C. Jennings, Dr. G. Knobloch, Prof. Dr. E. Kramer, L. G. Krauskopf,  
Dr. T. Kromminga, Dr. J. Jurja, C. Lavallee, D. Müller, Dr. D. Munteano,  
D. Ochs, Alfred G. Oertli, J.-R. Pauquet, R. Pfaendner, P. F. Ranken, Dr. E. Richter,  
Dr. P. Rota-Graziosi, R. Scherrer, Dr. A. Schmitter, Dr. K. Schwarzenbach,  
Prof. Dr. W. H. Starnes Jr., M. Thomas, Dr. G. Van Esche, Dr. H. J. Weideli,  
S. S. Woods, F. Wylin, J. Zingg

**HANSER**

Hanser Publishers, Munich

• Hanser Publications, Cincinnati

*The Editors:*

Dr. rer. nat. Hans Zweifel (†), Department of Materials, Institute of Polymers, ETH-Zentrum CNB E 38.2, Universitätstraße 41, CH-8092 Zurich, Switzerland

Dr. rer. nat. Ralph-Dieter Maier, Ciba Corporation, 540 White Plains Road, Tarrytown, NY 10591, USA

Dr. Michael Schiller, Chemson Polymer-Additive AG, Industriestraße 19, 9601 Arnoldstein, Austria

Distributed in the USA and in Canada by

Hanser Publications

6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA

Fax: (513) 527-8801

Phone: (513) 527-8896 or 1-800-950-8977

[www.hanserpublications.com](http://www.hanserpublications.com)

Distributed in all other countries by

Carl Hanser Verlag

Postfach 86 04 20, 81631 München, Germany

Fax: +49 (89) 98 48 09

[www.hanser.de](http://www.hanser.de)

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Plastics additives handbook / [edited by] Hans Zweifel. -- 6th ed. / [edited by] Ralph D. Maier, Michael Schiller.

p. cm.

ISBN 978-1-56990-430-5

1. Plastics--Additives. I. Zweifel, Hans, 1939-2001. II. Maier, Ralph D. III. Schiller, Michael. TP1142.P575 2008  
668.4'11--dc22

2008034203

Bibliografische Information Der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <<http://dnb.d-nb.de>> abrufbar.

ISBN 978-3-446-40801-2

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2009

Production Management: Steffen Jörg

Coverconcept: Marc Müller-Bremer, Rebranding, München, Germany

Coverdesign: MCP • Susanne Kraus GbR, Holzkirchen, Germany

Typeset: Kösel, Krugzell

Printed and bound by Kösel, Krugzell

Printed in Germany

## Preface to the Sixth Edition

Since the publication of its first edition 25 years ago, the Plastic Additives Handbook has widely been regarded as the ultimate publication in the world on plastic additives. In the new millennium, the then completely revised fifth edition has proven to be an essential reference. Because of its great success, the co-editors of the sixth edition left Hans Zweifel's fifth edition concept and structure in tact.

We felt that the technical content of the individual contributions are still current, so there was no need for a complete revision. The only exception is the chapter on PVC additives, an area in which legislation in the European Union and the United States is the driver of quick and drastic changes. These are reflected in the completely revised chapter, and historical, toxicological as well as new scientific aspects are discussed. We also brought back the chapter on plasticizers which had been left out of the fifth edition and is now included in the chapter on PVC additives.

In all chapters, the tables containing information on products and suppliers were updated and reflect the changes with respect to acquisitions, mergers and divestments in the world of plastic additives' producers that have happened since 2000. We also paid tribute to the internet boom that we witnessed during the last decade and provided the URLs of the additive manufacturers and providers instead of mailing addresses and telephone numbers. For quick and always up-to-date reference, a Comprehensive list of tradenames and suppliers is provided at the end of this handbook. This list is continuously being updated and is available on the internet. It is expected that this will add to the usefulness of the Handbook.

We would like to thank all authors who contributed the individual chapters. Special thanks to Dr. Christine Strohm with Hanser Publishers for her sponsorship and competence as well as to Ciba Corporation and Chemson GmbH for supporting our efforts to edit the Plastic Additives Handbook.

Tarrytown and Arnoldstein, November 2008

Ralph D. Maier  
Michael Schiller

# 1 Antioxidants

Dr. K. Schwarzenbach, Dr. B. Gilg, Dipl. Ing. D. Müller, Dr. G. Knobloch,  
Dipl. Ing. J.-R. Pauquet, Dr. P. Rota-Graziosi, Dr. A. Schmitter, J. Zingg,  
Ciba Inc., Additives Division, Basel, Switzerland  
Prof. Dr. E. Kramer, FH Aarau, Brugg-Windisch, Switzerland

## 1.1 Introduction

Organic materials, both of synthetic and natural origin, readily undergo reactions with oxygen [1]. Such oxidation reactions are of vital interest if the organic material is a polymer, because important properties often change at very low conversion ratio. For example, if the oxidation reaction leads to the chain scission of a linear polymer with 10000 monomer units, a conversion rate of 100 ppm is sufficient to halve the molecular weight of the polymer. When polymers oxidize, they lose mechanical properties, e.g., tensile strength, and rougher surface appearance and discoloration of the plastic article may result. Oxidation can occur in every stage of the life cycle of a polymer: during manufacture and storage of the polymer resin, as well as during processing and end use of the plastic article produced. Plastic materials are very different from each other in terms of their inherent sensitivity to oxidation. The oxidative sensitivity of polypropylene is apparent at room temperature while polystyrene and poly(methyl methacrylate) are quite stable even at processing temperatures. Highly unsaturated polymers, such as rubbers or copolymers derived from butadiene or isoprene, are extremely sensitive to oxidation.

The typical technical manifestations of oxidation are referred to as "aging phenomena"; the effects of oxidation on a polymer's chemical structure are collectively termed "degradation". Degradation and aging can be inhibited or retarded; methods of achieving this are the main topics of this chapter.

One method of inhibiting or slowing down thermal oxidation is to structurally modify the polymer, but by far more common is the use of suitable stabilizers. In this chapter, the behavior of plastics under thermomechanical (processing of polymer melt) as well as thermo-oxidative (long term stability during end use) conditions is discussed. Modern plastics parts and articles are complex systems that generally contain, along with the polymer, fillers, pigments, flame retardants, reinforcing materials, as well as a variety of other additives that can influence oxidative degradation reactions.

## 1.2 Economic Situation

The growth in volume and the economic importance of plastic additives have followed the growth of the plastics industry. Higher demands concerning the service life and quality (ISO 9000 series) of plastic goods and to increase manufacturing productivity by raising processing temperatures and speeds has led to greater needs for high performance stabilizers and additives.

## 2 Antioxidants

The use of antioxidants in the plastics industry is summarized in Tables 1.1, 1.2, and 1.3.

Most antioxidants are used in polyolefins; approximately 15% are used in styrenics and impact modified styrenics. Major engineering resins are polycarbonate, polyester, polyamide, and polyacetal. The type and volume of antioxidant used depends on the type of resin and application; typical loadings range from 0.05 to 1 % by weight. Suppliers of plastic additives are mainly major chemical companies with a focus on specialty markets.

**Table 1.1** Global consumption of antioxidants in plastics – 1997 (in 1000 t)  
(Philip Townsend Associates, Inc., with permission)

Antioxidant	North America	Europe	Asia/Pacific	ROW	Total 1000 t	% Of Total
BHT	5.5	8.0	10.0	5.0	28.5	14 %
Other phenolic	25.9	22.0	26.0	14.0	87.9	43 %
Total phenolic	31.4	30.0	36.0	19.0	116.4	56 %
Organophosphites	19.1	15.0	21.4	8.0	63.5	31 %
Thioesters	5.9	5.0	6.4	2.0	19.3	9 %
Others	1.1	4.0	0.2	2.0	7.3	4 %
Total	57.5	54.0	64.0	31.0	206.5	100 %

**Table 1.2** Global consumption of antioxidants in plastics – 1997 (in million US \$)  
(Philip Townsend Associates, Inc., with permission)

Antioxidant	North America	Eu-rope	Asia/Pacific	ROW	Total million \$	% Of Total
BHT	24.0	27.0	35.0	19.0	105.0	7 %
Other phenolic	200.0	195.0	223.0	146.0	764.0	53 %
Total phenolic	224.0	222.0	268.0	165.0	869.0	60 %
Organophosphites	126.0	124.0	155.0	25.0	430.0	30 %
Thioesters	22.0	18.0	33.5	10.0	83.5	6 %
Others	11.0	37.0	1.5	10.0	59.5	4 %
Total	383.0	401.0	448.0	210.0	1,442.0	100 %

**Table 1.3** Global consumption of antioxidants in plastics by resin – 1997 (in 1000 t)  
 (Philip Townsend Associates, Inc., with permission)

Resin	North America	Europe	Asia/Pacific	ROW	Total 1000 t	% Of Total
PP	22.4	21.8	26.0	12.0	82.0	40 %
PE	14.2	13.5	16.0	8.0	51.7	25 %
Styrenics	8.7	8.0	9.5	4.5	30.7	15 %
Engineering resins	5.7	5.5	6.5	3.0	20.7	10 %
PVC	3.0	2.7	3.0	1.5	10.2	5 %
Other	3.5	2.7	3.0	2.0	11.2	5 %
Total	57.5	54.0	64.0	31.0	206.5	100 %

## 1.3 Principles of Oxidative Degradation

### 1.3.1 Introduction

Numerous oxidation products are formed as the result of the degradation of polymers, such as peroxides, alcohols, ketones, aldehydes, acids, peracids, peresters, and  $\gamma$ -lactones. Elevated temperatures, irradiation, and catalysts such as metals and metal ions increase oxidation rates. Most polymers have structural elements that are particularly prone to oxidative degradation reactions.

Spectroscopic investigations show that degradation products contain the same functional groups as those formed by the oxidation of low molecular weight hydrocarbons.

Thermoplastic polymers are prepared by chain polymerization, polyaddition, or polycondensation reactions. Their subsequent processing, usually in several steps, results in commercial end products. During processing, the polymer is subjected to heat and mechanical shear. Finished articles often are designed to be used over many years with minimal changes in their chemical, physical and mechanical properties and esthetic aspects. However, oxygen, heat, light, and water are present throughout the whole life cycle of the plastic article. Under these conditions, polymer chains undergo cleaving by oxidation, chain branching, and/or crosslinking. Understanding oxidative degradation and its prevention is therefore fundamental to the plastics industry.

Aging phenomena can be caused by processes other than oxidation. First, crystallization or relaxation processes are observed in finished articles of temperatures below the plastic's melting point or glass transition. Such processes cause aging and can increase the sensitivity to oxidative degradation. Second, polyesters, polyamides, and polyurethanes may undergo degradation by chain scission through hydrolysis. Third, sensitivity to oxidation is also affected by fillers, pigments, reinforcing materials, and other additives.

## 4 Antioxidants

**1.3.2 Autoxidation**

Polymer oxidation was first investigated concerning the aging of natural rubber. Hoffmann [2] recognized the connection between rubber aging and the absorption of oxygen. The reaction of organic compounds with molecular oxygen later was called autoxidation, because such reactions often proceed automatically, whenever organic materials are exposed to the atmosphere. Autoxidation is characterized by two features: autocatalysis and inhibition by additives. These characteristics are typical for radical reactions (also called homolytic reactions), which, in turn, are almost invariably chain reactions. The autoxidation

**Chain initiation:****Chain propagation:****Chain branching:****Chain termination:**

**Scheme 1.1** General diagram of autoxidation; R stands for the polymer backbone.

reaction was first investigated by Bolland and Gee [3,4]. The results were rationalized as a free-radical initiated chain reaction which, as other radical reactions, can be regarded as proceeding by three types of reactions: chain initiation, chain propagation, and chain termination.

The origin of the primary alkyl radical  $R^*$  (Eq. 1.1) as the initiating species for the chain reaction is still not fully determined. Direct reaction of hydrocarbons with molecular oxygen in a bimolecular reaction is not favored because of thermodynamic and kinetic considerations. One explanation is that, in the course of polymerization, catalysts such as transition metals, radical initiators, impurities in the monomers, and minute amounts of oxygen react and form peroxy radicals  $ROO^*$  (Eq. 1.2) which abstract hydrogen from the polymer and form an alkyl radical (Eq. 1.3).

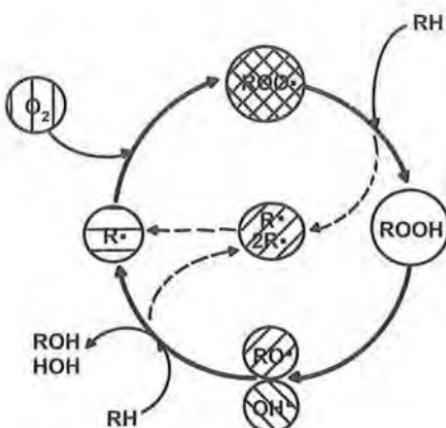
The technical preparation of "purest" polymer is simply not possible. Structural defects and impurities cannot be excluded. Furthermore, during the first processing step of the melt, e.g., extrusion, blow molding, or injection molding, additional peroxide radicals are formed by reaction with molecular oxygen under condition of heat and mechanical shear. Subsequently, these peroxy radicals become hydroperoxides upon abstraction of hydrogen (Eq. 1.3). The decomposition of hydroperoxides (Eq. 1.9) to alkoxy and hydroxyl radicals is a reaction with considerable activation energy. Thus, the rate increases with rising temperature. This reaction is further accelerated by light or metal ions.

Alkyl radicals react with molecular oxygen practically without activation energy, i.e., the reaction occurs at approximately the same rate at any temperature forming peroxy radicals.

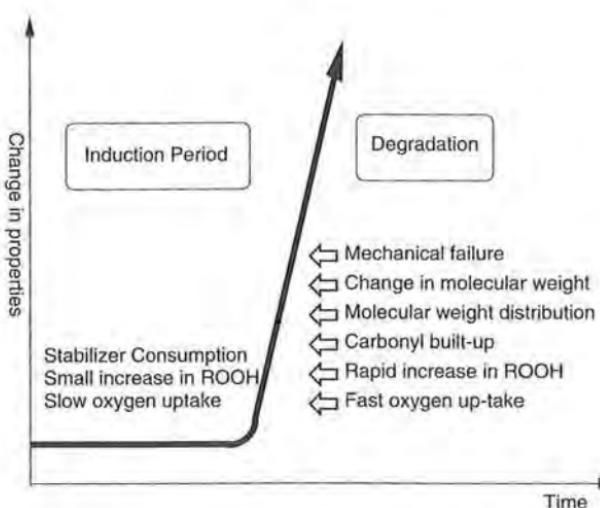
The rate constant for the reaction of most alkyl radicals<sup>1</sup> with oxygen [5] is of the order of  $10^7$ – $10^9 \text{ mol}^{-1} \text{s}^{-1}$ . The abstraction of a hydrogen, H, by a peroxy radical  $ROO^*$  (Eq. 1.3) requires the breaking of a C–H bond. This reaction requires activation energy and is the rate-determining step in autoxidation. Structurally, the rate of the abstraction reaction decreases in the following order: hydrogen in  $\alpha$ -position to a C=C double bond ("allyl") > benzyl hydrogen and tert. hydrogen > sec. hydrogen > prim. hydrogen [6, 7, 8, 9, 10, 11].

Primary and secondary peroxy radicals are more reactive than the analogous tertiary radicals [7,8] with regard to hydrogen abstraction. The most reactive are acylperoxy radicals [12]. If sufficient oxygen is available and the formation of peroxy radicals does not occur at too high temperature, then chain termination mainly proceeds according to Eq. 1.15 by recombination of peroxy radicals [13]. Under oxygen deficient conditions, i.e., when the concentration of  $[R^*]$  is much higher than that of  $[ROO^*]$ , chain termination is caused by recombination with other radical species available according to Eqs. 1.11 and 1.12. An important termination reaction is disproportionation of alkyl radicals, as shown by Eq. 1.14. The oxidative autocatalytic degradation reaction is slow at the start (induction period) and accelerates as the concentration of the resulting hydroperoxides increases (Schemes 1.2 and 1.3).

Of prime importance are those reactions, which lead to a change in such polymer properties as molecular weight and molecular weight distribution. These changes have immediate impacts on properties that determine the service life of the polymer. These changes are therefore the main reasons for premature material failure in an oxidative environment.



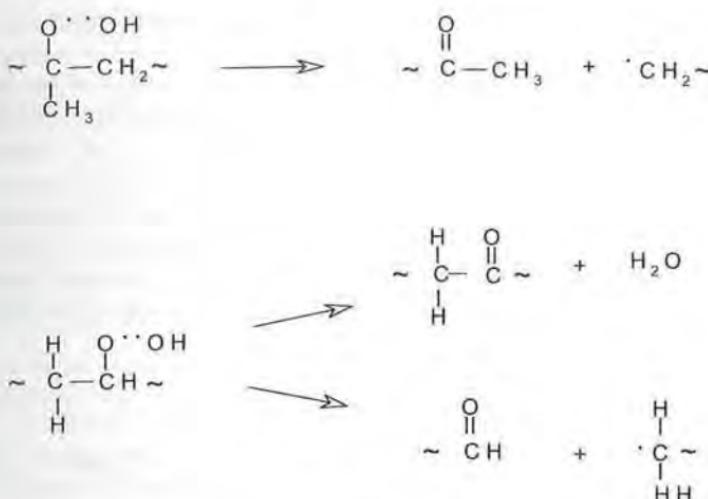
Scheme 1.2 The cycle of autoxidation



Scheme 1.3 Changes in material properties during aging of polymers

The most important propagation reaction leading to chain scission of the macromolecule is the so-called  $\beta$ -scission reaction (Eq. 1.7) of an alkoxy radical (Scheme 1.4).

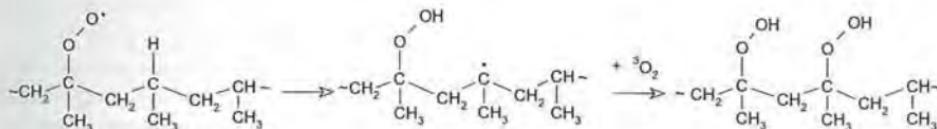
In the case of polyethylene, instead of the  $\beta$ -scission, an “in-cage” reaction of the secondary alkoxy radical, with the formation of a keto group, may occur (upper reaction, Scheme 1.4).  $\beta$ -scission reactions involving tertiary alkoxy radicals, as in the case of polypropylene, generally lead to chain scission of the macromolecule. Furthermore, in polypropylene and



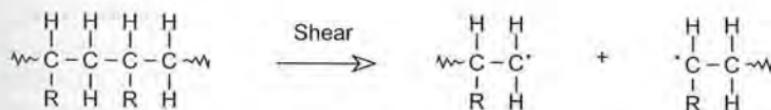
Scheme 1.4  $\beta$ -scission reaction involving secondary and tertiary alkoxy radicals

other polymers with branched alkanes as repeating units, e.g. polystyrene, the formation of hydroperoxide sequences on the polymer backbone is favored through a six-membered transition state (Scheme 1.5). This fact is why oxidative degradation occurs more readily in polypropylene compared to polyethylene.

In the course of polymer processing e.g., extrusion, the oxygen dissolved in the polymer melt is consumed rapidly and follow-up diffusion of oxygen is not possible. Therefore, the concentration of alkyl radicals,  $\text{R}^\bullet$ , is much greater than that of peroxy radicals,  $\text{ROO}^\bullet$ . Alkyl radical formation during polymer processing can also result from high shearing forces in the processing machines (Scheme 1.6).



Scheme 1.5 Reaction of molecular oxygen with a PP macroalkyl radical



Scheme 1.6 Alkyl radical formation during polymer processing